Supporting Information

Charge transfer state emission dynamics in blue-emitting functionalized silicon nanocrystals

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Experimental.

Materials. Hydrogen silsesquioxane (HSQ) was purchased from Dow Corning Corporation (Midland, MI) as FOx-17. Phosphorus pentachloride (PCl_5, 98%, Sigma-Aldrich), dodecylamine (98%, Sigma-Aldrich), ammonium bromide (99.99%, Sigma-Aldrich), hydrofluoric acid (HF, 49%, J. T. Baker), toluene (ACS grade, BDH), anhydrous toluene (Sigma-Aldrich), methanol (MeOH, ACS grade, Sigma-Aldrich), and ethanol (EtOH, ACS grade, Sigma-Aldrich) were used without further purification.

Synthesis of oxide-embedded silicon nanocrystals (Si NCs). Oxide-embedded Si NCs were prepared using previously established method. Briefly, solid HSQ (*ca*. 3 g) was placed in a quartz boat and transferred to a Lindberg Blue tube furnace and heated from ambient to a peak processing temperature of 1100 °C at 18 °C min^{-1} in a slightly reducing atmosphere (*i.e.*, 5% H_2/95% Ar). The sample was maintained at the peak processing temperature for one hour. Upon cooling to room temperature, the resulting amber solid was ground into a fine brown powder using an agate mortar and pestle. This yields oxide embedded Si NCs with an average diameter of *ca*. 3 nm (Composite **1**). To obtain larger particles, 1.0 g of **1** was transfered to a high temperature furnace (Sentro Tech Corp.) for further thermal processing under Argon atmosphere. The composite was heated to 1200 °C at 10 °C/min and maintained at that temparature for an hour and cooled to room temperature. This yielded Composite **2** consisting of Si NC exhibiting average diameters of *ca*. 6 nm embedded in silica matrix. To obtain Si NCs of *ca*. 8-9 nm diameter, composite **1** was heated in the high temperature furnace to 1300 ^{o}C at 10 °C/min under Argon atmosphere and maintained at that temparature for an hour and cooled to room temperature to yield Compoite **3**. The composites were stored in glass vials until further use.

Synthesis of hydride terminated Si NCs. Freestanding hydride terminated Si NCs were liberated from their oxide matrix *via* hydrofluoric acid (HF) etching. Approximately 0.30 g of the oxide-embedded Si NC composite was transferred to a polyethylene terephthalate beaker and 3 mL of deionized water, 95% EtOH, and 49% HF acid were added with stirring in subdued light. (Caution: Hydrofluoric acid can be extremely dangerous and must be handled with great care.) The resulting dark brown, cloudy mixture was stirred for one hour. Hydrophobic hydride terminated Si NCs were extracted from the aqueous etching mixture using three 20 mL toluene extractions. All remaining HF was neutralized using an excess of aqueous saturated solution of calcium chloride. The cloudy dark brown Si NC/toluene extracts were placed into glass test tubes and centrifuged using a low speed (7000 rpm) centrifuge for 5 minutes. After centrifugation, the toluene supernatant was decanted leaving a precipitate of hydride terminated Si NCs.

Synthesis of ammonia stabilized Si NCs. Freshly prepared hydride terminated Si NCs (from Composite **1** or **2**) were suspended in toluene (10 mL). Ammonium bromide (0.3 g) was sonicated in 10 mL toluene and added to the hydride terminated Si NC solution and vigorously stirred for 3 hours. The reaction mixture was centrifuged at 14000 rpm for 10 min and the supernatant containing ammonia stabilized Si NCs was collected.

Synthesis of dodecylamine functionalized Si NCs. Hydride terminated Si NCs obtained from composites **2** or **3** (larger particles are used as PCl_5 further etches the NC surface) were dispersed in 5 mL anhydrous toluene and transferred to a Schlenk flask containing 15 mL dry toluene. 0.35 g of PCl_5 was added to the hydride Si-NCs and stirred together for 90 minutes at 40 ^{o}C under Ar atmosphere. Toluene and byproducts including PCl_3 were removed *in vacuo* leaving an orange precipitate. Dry toluene (15 mL) was added to the reaction flask, followed by 0.25 g of dodecylamine. The reaction mixture was heated at 40 ^{o}C for 8 hours under an Ar atmosphere. The

flask was cooled to room temperature and the clear light yellow solution was transferred to a separatory funnel and washed with distilled water thrice to remove excess dodecylamine and hydrochloride salt. The toluene layer was filtered through a hydrophobic PTFE filter, and the particles were stored in glass vials until further use.

Figures

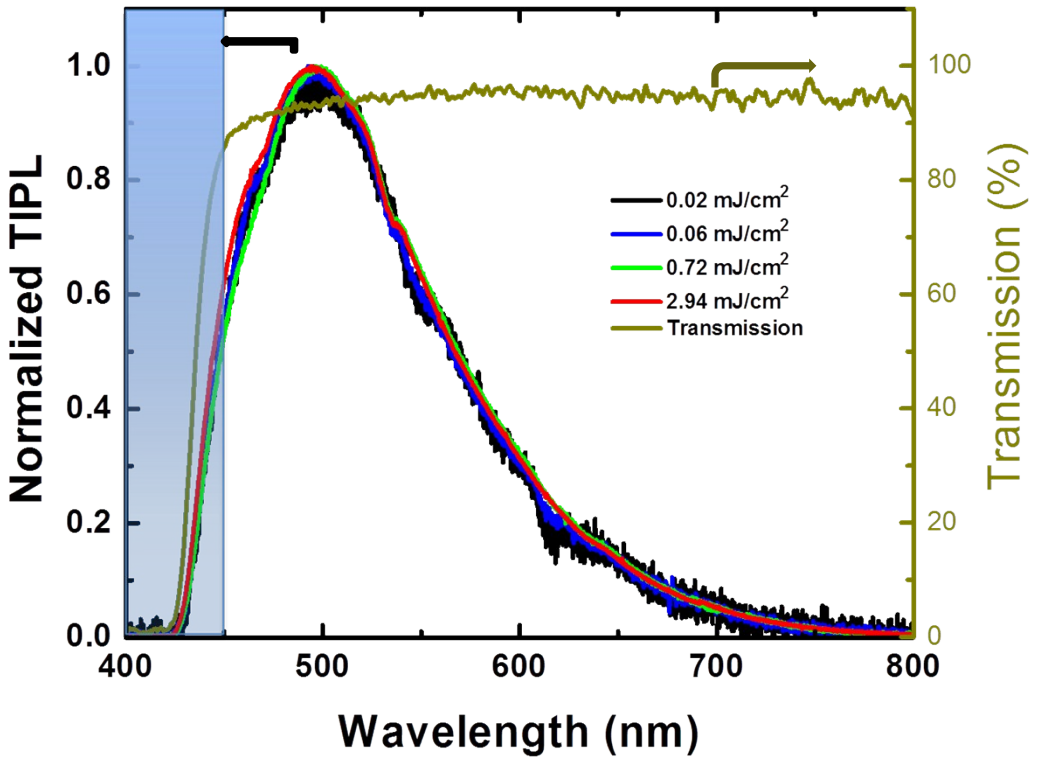

Fig. S1 Normalized fluence-dependent TIPL of 5.7-nm ammonia functionalized Si NCs. The yellow line shows the transmission spectrum of the long pass filter showing 86% transmission at 450 nm and a sharp decrease in transmission below 450 nm.

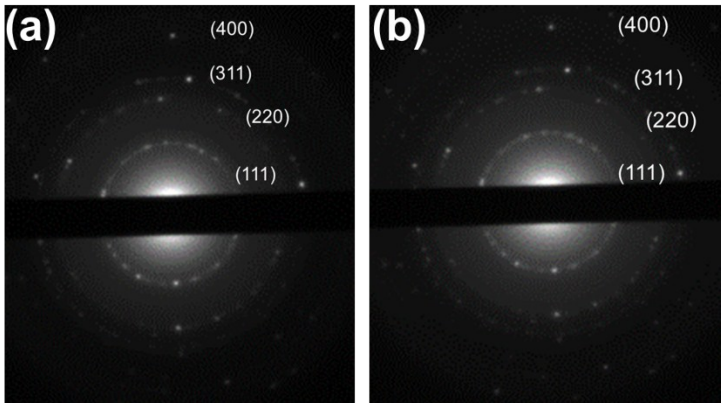

Fig. S2 Electron diffraction pattern of (a) ammonia and (b) dodecylamine Si NCs.

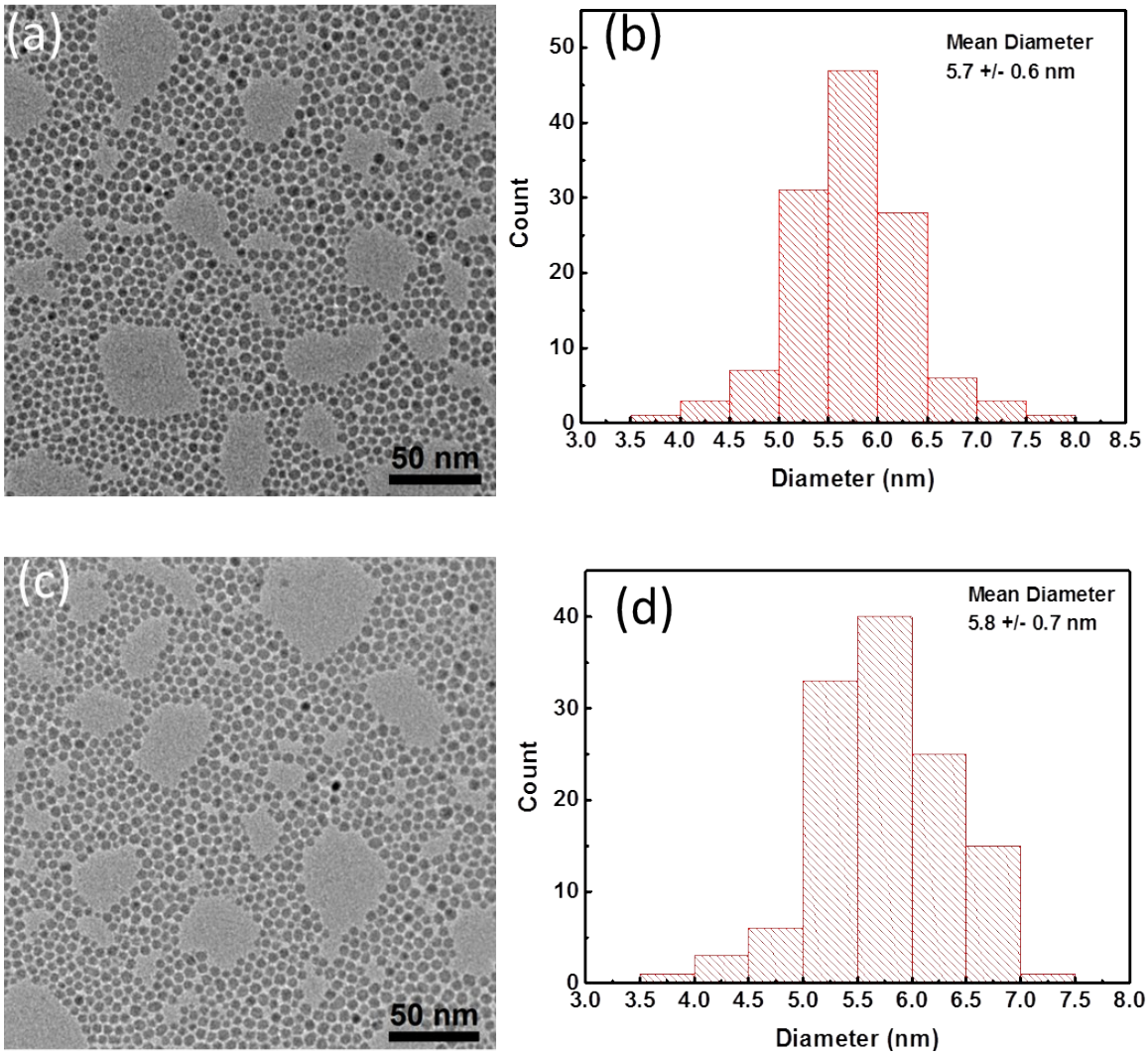

Fig. S3 TEM images of ~6 nm (a) ammonia and (b) dodecylamine functionalized Si NCs while (c) and (d) are their corresponding size distributions, respectively.

Table S1 Summary of the fit parameters according to Eq. 1 for spectrally-resolved PL dynamics of the functionalized Si NCs. The error in the lifetimes τ_1 and τ_2 is <0.006 ns. The error in the amplitude coefficients A_1 and A_2 is <0.005. The value of the constant offset, C (not listed here), ranges from 0.001 - 0.006.

Wavelength (nm)	Ammoia functionalized SiNCs								Dodecylamine functionalized SiNCs							
	3.4 nm				5.7 nm				3.1 nm				5.8 nm			
	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_1 (ns)	A_1	τ_2 (ns)	A_2
470	1.81	0.61	6.12	0.39	1.81	0.59	6.10	0.41	1.46	0.63	5.76	0.39	1.64	0.51	5.86	0.49
505	1.78	0.58	6.15	0.42	1.81	0.51	6.16	0.49	1.45	0.61	5.93	0.36	1.61	0.51	5.95	0.49
555	1.65	0.56	6.16	0.44	1.77	0.45	6.30	0.55	1.35	0.60	5.89	0.40	1.66	0.46	6.07	0.54
620	1.60	0.60	6.20	0.40	1.80	0.54	6.15	0.46	1.34	0.67	5.80	0.33	1.51	0.57	5.88	0.43

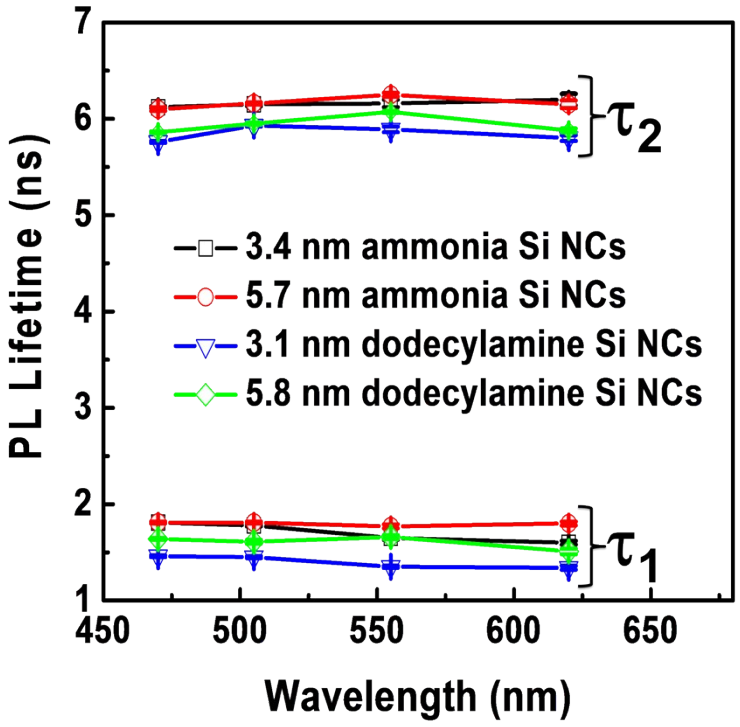

Fig. S4. Spectrally-resolved ns-PL dynamics of functionalized Si NCs.

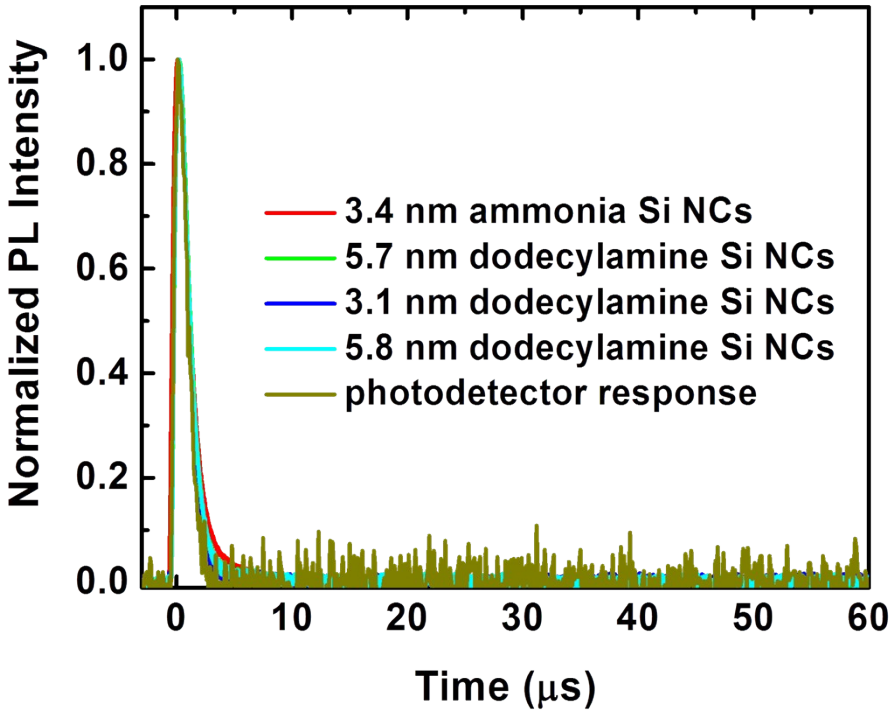

Fig. S5. Microsecond-TRPL measurements of the functionalized Si NCs at 560 nm using a fast Si photodetector. The photodetector response was measured using scattered light from the 400 nm excitation pulse.

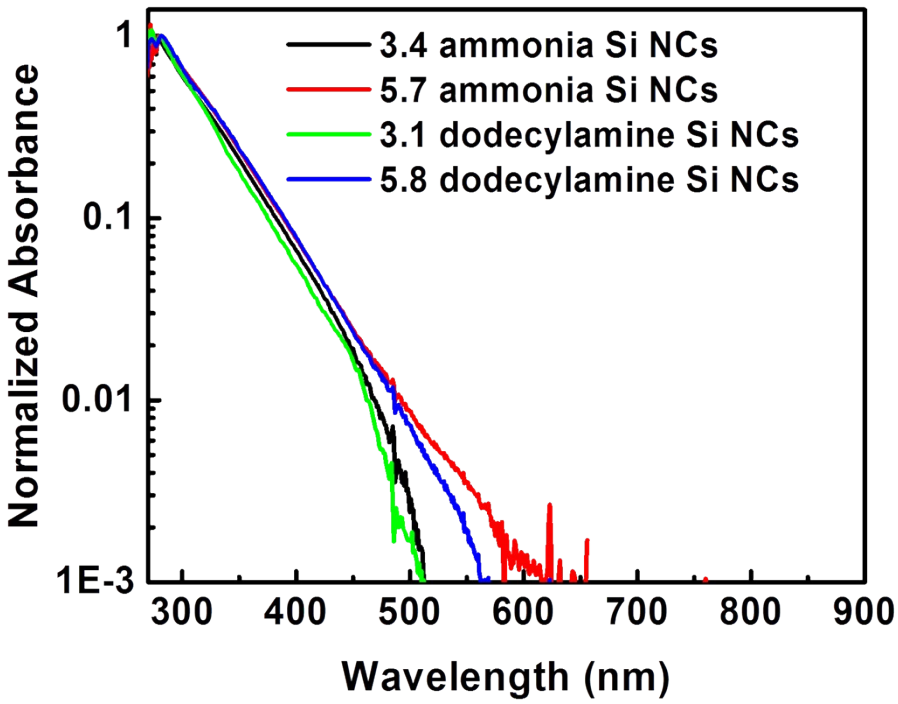

Fig. S6. Normalized absorbance of different sizes of functionalized Si NCs.